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Fourier transform microwave spectrum of pyridine–neon

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ABSTRACT

The rotational spectra of normal, and various ^{15}N, ^{13}C and ^{22}Ne species of pyridine–neon have been investigated by molecular beam Fourier transform microwave spectroscopy. The obtained results allowed for the experimental determination of the structure and of the ^{14}N quadrupole coupling constants of the complex. The spectroscopic parameters are compared to those of other rare gases–pyridine complexes.

1. Introduction

Several complexes of six-membered aromatic molecules with rare gases (RG) have been investigated by rotational spectroscopy. The rotational spectra of benzene–RG, with RG = Ne [1,2], Ar [2,3], Kr [4] and Xe [2] have been observed by Fourier transform microwave spectroscopy (FTMW) combined with pulsed jet techniques. Also in the case of pyridine, the rotational spectra of four pyridine–RG adducts have been measured, with FTMW spectroscopy for RG = He [5], Ar [6,7] and Kr [6], and with free jets mmw spectroscopy for RG = Ne [8] and Ar [9]. In addition, the free jets mmw spectra of pyrimidine–Ne [10], pyridazine–Ne [11] pyrimidine–Ar [12] and pyridazine–Ar [13] have been reported.

In all these cases, the RG atom is located on one side of the aromatic ring, and the barriers in going from above to below the aromatic planes are high enough to prevent tunnelling effects to be observed, except for some small splittings in the case of pyridine–He. Information on the van der Waals motions has been obtained. Generally the RG stretching motion has been considered isolated from the bending motions, and its frequency has been obtained from the D_J centrifugal distortion constant within a pseudo-diatomic approximation. From these frequencies, approximate values of dissociation energies have been obtained [8–13]. Also information on the bending motions has been obtained, either from centrifugal distortion constants [14], or from mass distribution and Coriolis effects [12].

It has been claimed that the π-electron systems of aromatic molecules play important roles in non-covalent interactions and that in rare gas atoms containing van der Waals systems, for example, the aromatic π-electrons provide a significant driving force for the weak intermolecular bond [5,15]. However, distributed polarizability models, based on contribution from dispersion interactions, the magnitude of which depends on the polarizability of the involved atoms or molecules, have been found very effective in finding van der Waals potential energy surfaces [16,17].

Here we report the FTMW spectra of several isotopologues of pyridine···Ne (from now on Pyr···Ne), and discuss the obtained results, that is the quadrupole coupling constants of ^{14}N and the structure of the complex.

The principal axis systems of Pyr ···Ne (left) and Pyr (right) are shown in Fig. 1.

2. Experimental part

The MB-FTMW spectrum in the 6–18.5 GHz frequency region was measured using a COBRA-type [18] pulsed supersonic jet Fourier transform microwave (FTMW) spectrometer [19] described elsewhere [20], recently updated with the FTMW++ set of programs [21]. Neon was passed over pyridine at room temperature, and the mixture was expanded from ca 3 bar to about 10^{-5} mbar. Each rotational line is split by the Doppler effect, enhanced by the molecular beam expansion in the coaxial arrangement of the supersonic jet and resonator axes. The rest frequency is calculated as the arithmetic mean of the frequencies of the Doppler components. The estimated accuracy of frequency measurements is better than 3 kHz and lines separated by more than 7 kHz are resolvable.

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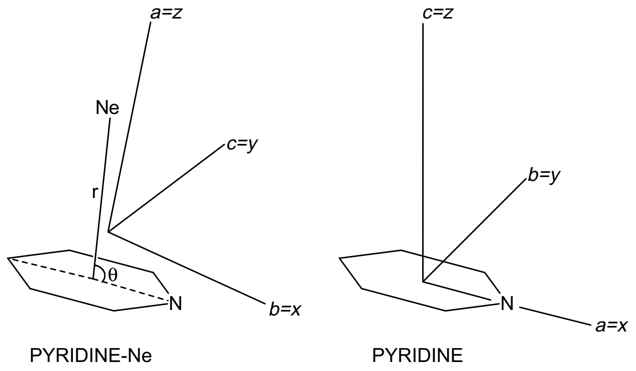

Fig. 1. Sketches of Pyr···Ne and Pyr showing the permutation of the principal axes in going from the isolated molecule to the complex. *R* and *θ* are the determined van der Waals parameters.

^{15}N-pyridine (99%) was obtained from Aldrich, and used without further purifications.

3. Rotational spectrum

From the rotational constants of Ref. [8] it was easy to locate the rotational transitions of the normal species of Pyr···Ne, falling in the 8–18 GHz frequency region of our FTMW spectrometer. Later on, the rotational spectra were assigned also for the additional six isotopologues with ^{22}Ne, ^{15}N, ^{15}N–$^{13}C(2)$, ^{15}N–$^{13}C(3)$, ^{15}N–$^{13}C(4)$ and ^{15}N–^{22}Ne isotopic substitutions. To measure the ^{13}C species in natural abundance, the ^{15}N-enriched pyridine was used, since their rotational transitions, not split for the quadrupole, are much stronger than the corresponding lines of the ^{14}N (normal) species.

Fig. 2 shows the ^{14}N-quadrupole hyperfine component lines of the 3_{13}–2_{02} transition of the normal species.

The frequencies of all measured lines are listed in Tables 1 and 2. The newly measured frequencies of the normal species, together with those previously measured in the millimeter wave range [8], for a total of 57 rotational lines, have been fitted with SPFIT Pickett program [22], according to the Hamiltonian:

$$\mathbf{H} = \mathbf{H}_R + \mathbf{H}_{CD} + \mathbf{H}_Q \qquad (1)$$

Table 1
Experimental transition frequencies (MHz) of Pyr^{14}N···Ne and one related isotopologue

$J'(K'_a,K'_c) \leftarrow J''(K''_a,K''_c)$	F'	F''	^{20}Ne	^{22}Ne
2(1,2)–1(0,1)	3	2	8584.6473	8310.4598
	2	1	8583.4040	8309.0130
	1	0	8586.5724	8312.1906
	2	2	8584.3823	8309.9938
	1	1	8584.1285	8309.7361
2(2,1)–1(1,0)	3	2		10798.1044
	2	1		10796.6183
	1	0		10799.3392
3(1,3)–2(0,2)	4	3	12289.8643	11833.8722
	3	2	12288.6157	11832.6195
	2	1	12290.5122	11834.5230
	3	3	12289.6444	11833.6544
	2	2	12288.9079	11832.9047
4(0,4)–3(1,3)	5	4	13840.8422	
	4	3	13842.0917	
	3	2	13840.4999	
4(1,4)–3(0,3)	5	4	15984.4745	15347.6154
	4	3	15983.3110	15346.4457
	3	2	15984.8697	15348.0144

where $\mathbf{H}_R$, $\mathbf{H}_{CD}$ and $\mathbf{H}_Q$ are the rotational, centrifugal distortion and ^{14}N quadrupole (when appropriate) contributes to the total Hamiltonian.

Since Pyr···Ne is a prolate near-symmetric top, the S-reduction and the I^r-representation have been chosen [23].

The same Hamiltonian has been used for the ^{22}Ne species, while for the ^{15}N-isotopologues, the $\mathbf{H}_Q$ component of the Hamiltonian has been omitted. All obtained spectroscopic constants are given in Table 3.

4. Structure

When choosing Pyr-^{15}N···Ne as parent molecule, it is possible to obtain, from the available experimental data, the r_s coordinates [24] of all heavy atoms of the complex in the principal axes system of Pyr-^{15}N···Ne. They are reported in Table 4. It appears clear that the $|c|$-coordinates of the N, C4 and Ne atoms, which should be zero by symmetry, have small imaginary value, probably because of the large amplitude van der Waals vibrations. They prove unambiguously that the Ne atom is considerably shifted towards the N

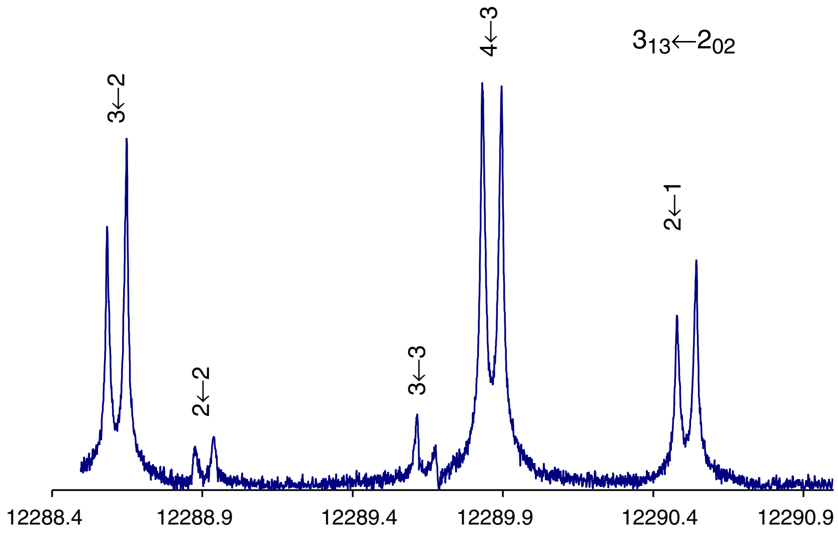

Fig. 2. The five $F' \leftarrow F''$ ^{14}N quadrupole component lines of the 3_{13}–2_{02} transition of normal Pyr···Ne. Each of them is split into two Doppler components.